JC07 Rec'd PCT/PTO 25 FEB 2002

FORM PTO-1390 (REV. 11-2000) — U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER	
0020-4960P	
U.S. APPLICATION NO. (If known, see 37 CFR 1.5)	
10/069345 NEW	

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/JP00/05674	August 24, 2000	August 25, 1999

TITLE OF INVENTION

METHOD FOR STABILIZING FLUORINE-CONTAINING COPOLYMER

APPLICANT(S) FOR DO/EO/US

IMANISHI, Hiroyuki; HIRAGA, Yoshiyuki; NAMIMATSU, Masayuki; KOMATSU, Satoshi

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1).
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☒ has been transmitted by the International Bureau. Wo 01/14430
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
   a. ☒ is transmitted herewith.
   b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4)
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 20. below concern document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98, Form PTO-1449(s), and International Search Report (PCT/ISA/210) with 0 cited document(s).
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
14. ☐ A SECOND or SUBSEQUENT preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821-1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:
    1.) PCT/IB/304 and PCT/IB/308
    2.) Zero (0) sheets of Formal Drawigns

U.S. APPLICATION NO (if known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUMBER
10/069345 NEW	PCT/JP00/05674	0020-4960P

21. ☒ The following fees are submitted:		CALCULATIONS	PTO USE ONLY
BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5):			
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO.	**$1,040.00**		
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO	**$890.00**		
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO.	**$740.00**		
International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4)	**$710.00**		
International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4).	**$100.00**		
ENTER APPROPRIATE BASIC FEE AMOUNT =		$ 890.00	
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).		$ 0	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total Claims	14 - 20 =	0	X **$18.00**	$ 0	
Independent Claims	1 - 3 =	0	X **$84.00**	$ 0	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)		Yes	+ **$280.00**	$ 280.00	
			TOTAL OF ABOVE CALCULATIONS =	$ 1170.00	
☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				$ 0	
			SUBTOTAL =	$ 1170.00	
Processing fee of **$130.00** for furnishing the English translation later than ☐20 ☐30 months from the earliest claimed priority date (37 CFR 1.492(f)).			+	$ 0	
			TOTAL NATIONAL FEE =	$ 1170.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property			+	$ 40.00	
			TOTAL FEES ENCLOSED =	$ 1210.00	
				Amount to be: refunded	$
				charged	$

a. ☒ A check in the amount of $ **1210.00** to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account. No. _____ in the amount of $_____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 02-2448.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

Send all correspondence to:
Birch, Stewart, Kolasch & Birch, LLP or Customer No. 2292
P.O. Box 747
Falls Church, VA 22040-0747
(703) 205-8000

Date: February 25, 2002

By _____
Andrew D. Meikle, #32,868

/cqc

PATENT
0020-4960P

IN THE U.S. PATENT AND TRADEMARK OFFICE

Applicant: IMANISHI, Hiroyuki et al.

Int'l. Appl. No.: PCT/JP00/05674

Appl. No.: New Group:

Filed: February 25, 2002 Examiner:

For: METHOD FOR STABILIZING FLUORINE-CONTAINING COPOLYMER

PRELIMINARY AMENDMENT

BOX PATENT APPLICATION
Assistant Commissioner for Patents
Washington, DC 20231

February 25, 2002

Sir:

The following Preliminary Amendments and Remarks are respectfully submitted in connection with the above-identified application.

AMENDMENTS

IN THE SPECIFICATION:

Please amend the specification as follows:

Before line 1, insert --This application is the national phase under 35 U.S.C. § 371 of PCT International Application No. PCT/JP00/05674 which has an International filing date of August 24, 2000, which designated the United States of America.--

IN THE CLAIMS:

Please amend the claims as follows:

4. (Amended) The method for stabilizing a melt-processable fluorine-containing copolymer according to claim 1 or 2, wherein said fluorine-containing copolymer is a copolymer of at least two monomers selected from the group consisting of tetrafluoroethylene, hexafluoropropylene, perfluoroalkyl vinyl ethers, ethylene and vinylidene fluoride.

6. (Amended) The method for stabilizing a melt-prcessable fluorine-containing copolymer according to claim 1 or 2, wherein said fluorine-containing copolymer is heated to a temperature of 360 to 430°C for 10 minutes or less before reheating.

7. (Amended) The method for stabilizing a melt-prcessable fluorine-containing copolymer according to claim 1 or 2, wherein said fluorine-containing copolymer has a melt viscosity of 0.1 to 100 kPa.s at 372°C.

8. (Amended) The method for stabilizing a melt-processable fluorine-containing copolymer according to claim 1 to 2, wherein the reheating in the closed apparatus is continuously carried out.

REMARKS

The specification has been amended to provide a cross-reference to the previously filed International Application.

The claims have been amended to correct improper multiple dependent claims and to place the application into better form for examination. Entry of the above amendments is earnestly solicited. An early and favorable first action on the merits is earnestly solicited.

Attached hereto is a marked-up version of the changes made to the application by this Amendment.

If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees required under 37 C.F.R. § 1.16 or under 37 C.F.R. § 1.17; particularly, extension of time fees.

Respectfully submitted,

BIRCH, STEWART, KOLASCH & BIRCH, LLP

By _____
Andrew D. Meikle, #32,868

P.O. Box 747
Falls Church, VA 22040-0747
(703) 205-8000

ADM/cqc
0020-4960P

Attachment: VERSION WITH MARKINGS TO SHOW CHANGES MADE

VERSION WITH MARKINGS TO SHOW CHANGES MADE

The claims have been amended as follows:

4. (Amended) The method for stabilizing a melt-processable fluorine-containing copolymer according to [any one of claims 1 to 3]claim 1 or 2, wherein said fluorine-containing copolymer is a copolymer of at least two monomers selected from the group consisting of tetrafluoroethylene, hexafluoropropylene, perfluoroalkyl vinyl ethers, ethylene and vinylidene fluoride.

6. (Amended) The method for stabilizing a melt-prcessable fluorine-containing copolymer according to [any one of claims 1 to 5]claim 1 or 2, wherein said fluorine-containing copolymer is heated to a temperature of 360 to 430°C for 10 minutes or less before reheating.

7. (Amended) The method for stabilizing a melt-prcessable fluorine-containing copolymer according to [any one of claims 1 to 6]claim 1 or 2, wherein said fluorine-containing copolymer has a melt viscosity of 0.1 to 100 kPa.s at 372°C.

8. (Amended) The method for stabilizing a melt-processable fluorine-containing copolymer according to [any one of claims 1 to 7]claim 1 to 2, wherein the reheating in the closed apparatus is continuously carried out.

DESCRIPTION

METHOD FOR STABILIZING FLUORINE-CONTAINING COPOLYMER

Field of the Invention

The present invention relates to a method for stabilizing a fluorine-containing copolymer. In particular, the present invention relates to a method for improving the thermal stability of a melt-processable fluorine-containing copolymer.

Background Art

For example, when an emulsion polymerized copolymer of tetrafluoroethylene and hexafluoropropylene is melt processed to obtain a final product, bubbles or voids may form due to volatile materials in the final product. The volatile materials are generated from polymer chain terminals and polymer backbones which are unstable against heat and/or shear force. If such unstable sites are stabilized during melt processing, the volatile materials still remain in the polymer processed, and thus the bubbles and voids may form when the polymer is processed to the final product.

JP-A-56-44883 discloses a method for reducing the content of volatile materials in a tetrafluoroethylene-hexafluoropropylene copolymer to 70 % or less of the initial content of the volatile materials by heating the copolymer which is statically placed on a pan or a mesh in an open condition, for example, in an electric furnace. However, the treatment in the open condition can hardly avoid the migration of foreign materials from outside to the heating process. Although the content of the volatile materials can be reduced by static heating, when the

filling depth of the copolymer increases, the treating time is prolonged with the influence of diffusion of the volatile materials, and also the treatment inside the layer of the copolymer filled becomes less uniform. To decrease the filling depth of the copolymer, a dish or a mesh having a large area is necessary. As a result, a large apparatus is required.

Disclosure of the Invention

An object of the present invention is to provide a method for effectively decreasing the content of volatile materials in a melt-processable fluorine-containing copolymer, which has been once molten, without using a large apparatus while avoiding the contamination of the copolymer with foreign particles.

According to the present invention, the above object is achieved by a method for stabilizing a melt-processable fluorine-containing copolymer comprising heating and melting the copolymer and then reheating the copolymer in a closed apparatus under a non-static condition, whereby a content of volatile materials in the copolymer is reduced to 30 % or less of an initial content of volatile materials.

The "content of volatile materials" used herein is expressed by a percentage (%) of a weight loss of the copolymer after heating the dried copolymer at 380°C under an absolute pressure of about 10 mmHg for 30 minutes based on the weight of the dried copolymer before heating.

The melt-processable fluorine-containing copolymer to be treated by the method of the present invention may be any one of known melt-processable fluorine-containing copolymers. Examples of the melt-processable copolymer include copolymers of

at least two monomers selected from the group consisting of tetrafluoroethylene (TFE), hexafluoropropylene (HFP), perfluoroalkyl vinyl ethers, ethylene (E) and vinylidene fluoride (VdF), vinylidene fluoride homopolymer, etc. In particular, a TFE-HFP-perfluoroalkyl vinyl ether copolymer containing 8 to 25 % by weight of HFP and 0 to 5 % by weight of the perfluoroalkyl vinyl ether is preferable.

Here, the perfluoroalkyl vinyl ether is preferably a vinyl ether of the formula:

$$CF_2=CFO(CF_2)_mF$$

wherein m is a number of 1 to 6, or the formula:

$$CF_2=CF[O-CF_2CF(CF_3)]_nOC_3F_7$$

wherein n is a number of 1 to 4.

The melt-processable fluorine-containing copolymer is preferably prepared from the above monomers by emulsion or suspension polymerization.

When the copolymer is a tetrafluoroethylene-hexafluoropropylene copolymer (FEP), a TFE-perfluoroalkyl vinyl ether copolymer (PFA) or a TFE-HFP-perfluoroalkyl vinyl ether copolymer, it preferably has a melt viscosity of 0.1 to 100 kPa.s at 372°C.

In one preferable embodiment, the method of the present invention includes two-step treatment comprising the steps of heating the fluorine-containing copolymer at a temperature of 360 to 430°C for 10 minutes or less to melt the copolymer, and then reheating the copolymer at a temperature from 130°C to the melting point of the fluorine-containing copolymer, preferably from 150°C to the melting point of the fluorine-containing copolymer.

The first heating step may comprise heating the copolymer with an extruder or heating the copolymer which is statically placed on a dish in an electric furnace equipped with a means to avoid the migration of foreign materials into the furnace.

When the temperature in the first heating step is lower than 360°C, the unstable sites at the copolymer chain terminals and in the copolymer backbones are not sufficiently stabilized. Therefore, even if the copolymer is reheated in the second step to decrease the content of the volatile materials, the copolymer may be bubbled in the melt processing of the copolymer to produce the final product.

In the method of the present invention, the heating in the second step can decrease the content of the volatile materials while maintaining the figure of the fluorine-containing copolymer which has been molten in the first step and shaped in a desired figure.

The heating in the second step is carried out in a temperature range from 130°C to the melting point of the fluorine-containing copolymer according to the relationship:

$$\log t = 6.12 - 0.0119T$$

wherein t is a treating time (hours) and T is a treating temperature (absolute temperature K)

to reduce the volatile materials.

When the temperature in the second step is lower than 130°C, the treating time is extended, and furthermore the volatile materials are not sufficiently decreased.

When the heating in the second step is continuously carried out, hot air flowing at a superficial velocity of 0.8 m/sec. or

less, preferably 0.05 to 0.5 m/sec. is used as a heating source, or such hot air is used in combination with heat conduction from the equipment wall.

When the heating in the second step is continuously carried out, preferably a residence time in the apparatus is controlled uniformly, and the properties of the product exited from the apparatus are made uniform.

In the case of continuously charging and discharging the copolymer, when the superficial velocity of the hot air exceeds 0.8 m/sec., the copolymer may be floated and mixed under the influence of the air flow and pressure of the hot air and thus it may become difficult to carry out the heating so that the copolymer uniformly containing the volatile materials is obtained.

The heating apparatus used in the present invention is not an open one but is a closed one which is closed during heating. The apparatus may be a vertical one or a horizontal one.

Herein, the "closed apparatus" means, either in a continuous process or in a batch process, an apparatus the interior atmosphere of which is not in direct contact with outside atmosphere during heating, and into which, only an air containing the controlled number of foreign materials having the limited maximum particle size is introduced through a filter, etc. except a part through which the copolymer is introduced in and removed from the apparatus. That is, it is not necessary to completely shield the interior atmosphere from the outside atmosphere (atmospheric air).

Herein, the term " non-static condition" is used to exclude the heating of the copolymer which is statically placed in a

container such as a dish. For example, in the case of a continuous process, this term means a condition of a moving layer such that the particles of the copolymer are filled in the apparatus in a layered state, and they continuously move through the apparatus according to the feeding rate of the copolymer and finally exit from the apparatus. In the case of a batch process, this term means a state where the copolymer is forcibly floated or fluidized with an agitator, etc.

The apparatus used for reheating may be a batch type one or a continuous type. A temperature distribution and the distribution of a decreasing rate of the volatile material can be controlled in relatively narrow ranges by continuously charging and discharging the copolymer, and thus the fluorine-containing copolymer which does not suffer from bubbling can be constantly produced.

In the case of a vertical continuous apparatus, a moving layer type one is advantageous, in which the copolymer is charged to an upper part of the apparatus and heated while it moves from the upper part to the lower part, and then it exits from the lower part of the apparatus. In the case of a horizontal batch apparatus, it is efficient to fluidize the fluorine-containing copolymer with an agitator such as a hot-air drier, a heat conduction-transfer drier, etc.

The migration of the foreign materials from outside can be prevented by forcibly supplying hot air to heat the copolymer in the closed apparatus. In the case of the moving layer type vertical apparatus for continuous processing, for example, rotary valves are provided at a charging part and a discharging part and

the interior pressure is made slightly higher than the atmospheric pressure, whereby the migration of the foreign materials into the apparatus can be prevented.

Furthermore, a apparatus for continuously cooling the fluorine-containing copolymer may be installed downstream the reheating apparatus to cool the copolymer to a temperature, at which the copolymer is finally shipped, or lower, for example, 60°C or lower.

Examples

The present invention will be illustrated by the following examples.

Hereinafter, the "content of volatile materials" is expressed by a percentage (%) of a weight loss of the copolymer after heating the dried copolymer at 380°C under an absolute pressure of about 10 mmHg for 30 minutes based on the weight of the dried copolymer before heating.

The bubbling test is carried out by heating a molded sheet of the copolymer having a thickness of 2.0 mm at 300°C for 10 minutes to melt the sheet. When the generation of bubbles in the sheet is observed with an eye, it is ranked "Bubbling", while the generation of bubbles is not observed, it is ranked "No bubbling".

The presence of foreign materials is evaluated by observing the presence of the foreign materials in a disc-shape sheet having a thickness of about 3 mm and a diameter of 120 mm, which is molded at 370°C.

Example 1

A TFE-HFP-perfluoropropyl vinyl ether copolymer, which was prepared by suspension polymerization, was used as a

fluorine-containing copolymer.

This copolymer had a melt viscosity of 2.3 kPa.s, a content of volatile materials of 0.88 % by weight before extrusion, a HFP content of 11.5 % by weight, and a content of perfluoropropyl vinyl ether of 0.9 % by weight.

The copolymer was washed and dried, and then extruded at a residence time of 2 minutes at 370°C with a single screw extruder having an inner diameter of 95 mm and a L/D ratio of 30. The extruded fluorine-containing copolymer was pelletized with a pelletizer, and then continuously charged and reheated in a moving layer, which was designed so that a residence time was 5 hours at 200°C. Hot air as a heat source was continuously supplied to a reheating apparatus at a superficial velocity of 0.35 m/sec. after removing foreign materials with passing the hot air through a filter (cutting 99.97 % of 3 μm particles).

The reheating apparatus had a height of 3,650 mm and an inner diameter of 850 mm. A cone-form punching metal was provided at the lower part of the apparatus to separate a hot air inlet from the moving layer. Thereby, the discharging of the pellets was facilitated.

The pellets, which were continuously discharged from the reheating apparatus, were then charged in a cooling apparatus and cooled to 60°C or lower, and continuously collected.

The pellets, which were collected from the cooling apparatus, contained 0.23 % by weight of the volatile materials, which was 26 % of the initial content of the volatile materials (0.88 % by weight). In the bubbling test, no bubble was observed, and no foreign material was contained in the pellets.

Comparative Example 1

The pellets, which were collected after extrusion and before reheating in Example 1, had a content of volatile materials of 0.75 % by weight, and bubbles formed in the bubbling test.

Comparative Example 2

The pellets, which were collected after extrusion and before reheating in Example 1, were statically placed on a dish in an electric furnace in a depth of about 20 mm and reheated at 200°C for 5 hours. The content of the volatile materials after reheating was 0.31 % by weight. That is, the content of the volatile materials decreased to 35 % of the initial content of the volatile materials and thus no bubble formed in the bubbling test. However, the pellets were contaminated with foreign materials from outside in the reheating step in the electric furnace, and a plurality of black foreign particles were observed with an eye.

The above results are summarized in Table 1.

Table 1

	Content of volatile materials [percentage based on initial content of volatile materials]	Presence of foreign materials	Bubbling test
Ex. 1	0.23 wt. % [26 %]	No	No bubbling
C. E. 1	0.75 wt. % [85 %]	No	Bubbling
C. E. 2	0.31 wt. % [35 %]	Yes	No bubbling

Example 2

The same fluorine-containing copolymer as one used in Example 1 was extruded with a single screw extruder having an inner diameter of 95 mm and a L/D ratio of 30 at 375°C at a residence time of 2 minutes. The extruded pellets were conveyed with an air which was passed through a filter (cutting 99.97 % of 3 μm

particles) so that the pellets were not in direct contact with the outside atmosphere, and continuously charged in a moving layer, which was designed so that a residence time was 1.5 hours at 235°C, and reheated with a hot air under the same conditions as those in Example 1.

The pellets discharged from the extruder had a content of volatile materials of 0.14 % by weight, which was 16 % of the initial content of the volatile materials. No bubbling was observed in the bubbling test.

Comparative Example 3

The pellets, which were collected after extrusion and before reheating in Example 2, had a content of volatile materials of 0.68 % by weight, and bubbles formed in the bubbling test.

Comparative Example 4

The pellets, which were collected after extrusion and before reheating in Example 2, were statically placed on a dish in an electric furnace in a depth of about 150 mm and reheated at 235°C for 1.5 hours.

The content of the volatile materials in the upper part of the accumulated pellets (a depth of 25 mm from the surface of the accumulated layer of the pellets) was 0.18 % by weight, and no bubble formed in the bubbling test.

However, the content of the volatile materials in the lower part of the accumulated pellets near the dish (a layer of 0 to 30 mm from the bottom surface of the dish) was 0.41 % by weight. That is, the content of the volatile materials was decreased only to 47 % of the initial content of the volatile materials, and bubbling was observed in the bubbling test. This is because the

thickness of the pellet layer filled in the dish was large, and the influence of diffusion of volatile materials could not be negligible so that the volatile materials could not be reduced in the lower part in the dish.

Like Comparative Example 2, the pellets were contaminated with foreign materials from outside in the reheating step in the electric furnace, and a plurality of black foreign particles were observed with an eye. The foreign particles were found not only in the upper part but also in the lower part.

The results in Example 2 and Comparative Examples 3-4 are summarized in Table 2.

Table 2

	Content of volatile materials [percentage based on initial content of volatile materials]	Presence of foreign materials	Bubbling test
Ex. 2	0.14 wt. % [16 %]	No	No bubbling
C. E. 3	0.68 wt. % [77 %]	No	Bubbling
C. E. 4 (upper part)	0.19 wt. % [22 %]	Yes	No bubbling
C. E. 4 (lower part)	0.41 wt. % [47 %]	Yes	Bubbling

Comparative Example 5

The pellets, which were extrusion molded in the same way as in Example 2, were continuously charged to a moving layer in a vertical cylinderical apparatus, which was designed so that a residence time was 24 hours at 120°C, to reheat the pellets. Hot air as a heat source was continuously supplied to the cylindrical apparatus at a superficial velocity of 0.40 m/sec. after passing the hot air through a filter (cutting 99.97 % of 3 μm particles).

The pellets discharged from the cylindrical apparatus had a content of volatile materials of 0.56 % by weight. Thus, the content of volatile materials decreased only to 64 % of the initial content of volatile materials, and bubbling was observed in the bubbling test.

CLAIMS

1. A method for stabilizing a melt-processable fluorine-containing copolymer comprising heating and melting said copolymer and then reheating said copolymer in a closed apparatus under a non-static condition, whereby a content of volatile materials in the copolymer is reduced to 30 % or less of an initial content of volatile materials.

2. The method for stabilizing a melt-processable fluorine-containing copolymer according to claim 1, wherein a reheating temperature is from 130°C to a melting point of said fluorine-containing copolymer.

3. The method for stabilizing a melt-processable fluorine-containing copolymer according to claim 1 or 2, wherein the reheating step is carried out with suppressing migration of foreign materials from outside to said closed apparatus.

4. The method for stabilizing a melt-processable fluorine-containing copolymer according to any one of claims 1 to 3, wherein said fluorine-containing copolymer is a copolymer of at least two monomers selected from the group consisting of tetrafluoroethylene, hexafluoropropylene, perfluoroalkyl vinyl ethers, ethylene and vinylidene fluoride.

5. The method for stabilizing a melt-processable fluorine-containing copolymer according to claim 4, wherein said fluorine-containing copolymer is a tetrafluoroethylene-hexafluoropropylene-perfluoroalkyl vinyl ether copolymer containing 8 to 25 % by weight of hexafluoropropylene and 0 to 5 % by weight of the perfluoroalkyl vinyl ether.

6. The method for stabilizing a melt-processable

fluorine-containing copolymer according to any one of claims 1 to 5, wherein said fluorine-containing copolymer is heated at a temperature of 360 to 430°C for 10 minutes or less before reheating.

7. The method for stabilizing a melt-processable fluorine-containing copolymer according to any one of claims 1 to 6, wherein said fluorine-containing copolymer has a melt viscosity of 0.1 to 100 kPa.s at 372°C.

8. The method for stabilizing a melt-processable fluorine-containing copolymer according to any one of claims 1 to 7, wherein the reheating in the closed apparatus is continuously carried out.

ABSTRACT

After a melt-processable fluorine-containing copolymer is heated and molten, the copolymer is reheatd in a closed apparatus under a non-static condition at a temperature of, for example, 130°C to the melting point of the fluorine-containing polymer, whereby a content of volatile materials in the copolymer is reduced to 30 % or less of an initial content of volatile materials. Thereby, the content of volatile materials in the melt-processable fluorine-containing copolymer, which has been once molten, can be effectively decreased without using a large apparatus while avoiding the contamination of the copolymer with foreign particles.

0020-4960P
Attorney Docket No.

BIRCH, STEWART, KOLASCH & BIRCH, LLP

P.O. Box 747 • Falls Church, Virginia 22040-0747
Telephone: (703) 205-8000 • Facsimile: (703) 205-8050

PLEASE NOTE: YOU MUST COMPLETE THE FOLLOWING

COMBINED DECLARATION AND POWER OF ATTORNEY FOR PATENT AND DESIGN APPLICATIONS

As a below named inventor, I hereby declare that: my residence, post office address and citizenship are as stated next to my name; that I verily believe that I am the original, first and sole inventor (if only one inventor is named below) or an original, first and joint inventor (if plural inventors are named below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Insert Title: METHOD FOR STABILIZING FLUORINE-CONTAINING COPOLYMER

Fill in Appropriate Information - For Use Without Specification Attached:

the specification of which is attached hereto. If not attached hereto,
the specification was filed on _____ as
United States Application Number _____;
and amended on _____ (if applicable) and/or
the specification was filed on August 24, 2000 as PCT
International Application Number PCT/JP00/05674; and was
amended under PCT Article 19 on _____ (if applicable)

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I do not know and do not believe the same was ever known or used in the United States of America before my or our invention thereof, or patented or described in any printed publication in any country before my or our invention thereof or more than one year prior to this application, that the same was not in public use or on sale in the United States of America more than one year prior to this application, that the invention has not been patented or made the subject of an inventor's certificate issued before the date of this application in any country foreign to the United States of America on an application filed by me or my legal representative or assigns more than twelve months (six months for designs) prior to this application, and that no application for patent or inventor's certificate on this invention has been filed in any country foreign to the United States of America prior to this application by me or my legal representatives or assigns, except as follows.

I hereby claim foreign priority benefits under Title 35, United States Code, §119(a)-(d) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Insert Priority Information: (if appropriate)

Prior Foreign Application(s)			Priority Claimed	
238250/1999 (Number)	Japan (Country)	Aug. 25, 1999 (Month/Day/Year Filed)	☑ Yes	☐ No
(Number)	(Country)	(Month/Day/Year Filed)	☐ Yes	☐ No
(Number)	(Country)	(Month/Day/Year Filed)	☐ Yes	☐ No
(Number)	(Country)	(Month/Day/Year Filed)	☐ Yes	☐ No

I hereby claim the benefit under Title 35, United States Code, §119(e) of any United States provisional applications(s) listed below.

Insert Provisional Application(s): (if any)

(Application Number)	(Filing Date)
(Application Number)	(Filing Date)

All Foreign Applications, if any, for any Patent or Inventor's Certificate Filed More than 12 Months (6 Months for Designs) Prior to the Filing Date of This Application:

Insert Requested Information: (if appropriate)

Country	Application Number	Date of Filing (Month/Day/Year)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States and/or PCT application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States and/or PCT application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose information which is material to the patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

Insert Prior U.S. Application(s): (if any)

(Application Number)	(Filing Date)	(Status - patented, pending, abandoned)
(Application Number)	(Filing Date)	(Status - patented, pending, abandoned)

0020-4960P

Attorney Docket No.

I hereby appoint the following attorneys to prosecute this application and/or an international application based on this application and to transact all business in the Patent and Trademark Office connected therewith and in connection with the resulting patent based on instructions received from the entity who first sent the application papers to the attorneys identified below, unless the inventor(s) or assignee provides said attorneys with a written notice to the contrary:

Raymond C. Stewart	(Reg. No. 21,066)	Terrell C. Birch	(Reg. No. 19,382)
Joseph A. Kolasch	(Reg. No. 22,463)	James M. Slattery	(Reg. No. 28,380)
Bernard L. Sweeney	(Reg. No. 24,448)	Michael K. Mutter	(Reg. No. 29,680)
Charles Gorenstein	(Reg. No. 29,271)	Gerald M. Murphy, Jr.	(Reg. No. 28,977)
Leonard R. Svensson	(Reg. No. 30,330)	Terry L. Clark	(Reg. No. 32,644)
Andrew D. Meikle	(Reg. No. 32,868)	Marc S. Weiner	(Reg. No. 32,181)
Joe McKinney Muncy	(Reg. No. 32,334)	Donald J. Daley	(Reg. No. 34,313)
John W. Bailey	(Reg. No. 32,881)	John A. Castellano	(Reg. No. 35,094)
Gary D. Yacura	(Reg. No. 35,416)		

Send Correspondence to:

BIRCH, STEWART, KOLASCH & BIRCH, LLP or **Customer No. 2292**

P.O. Box 747 • Falls Church, Virginia 22040-0747

Telephone: (703) 205-8000 • Facsimile: (703) 205-8050

PLEASE NOTE: YOU MUST COMPLETE THE FOLLOWING: ↓

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full Name of First or Sole Inventor: Insert Name of Inventor → Insert Date This Document is Signed → Insert Residence Insert Citizenship → Insert Post Office Address →

GIVEN NAME/FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
Hiroyuki IMANISHI	Hiroyuki Imanishi	Feb. 20, 2002
Residence (City, State & Country) JPY	CITIZENSHIP	
Settsu-shi, Osaka, Japan	Japan	
POST OFFICE ADDRESS (Complete Street Address including City, State & Country) c/o Yodogawa Works of DAIKIN INDUSTRIES, LTD., 1-1, Nishihitotsuya, Settsu-shi, Osaka 566-8585 Japan		

Full Name of Second Inventor, if any: see above

GIVEN NAME/FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
Yoshiyuki HIRAGA	Yoshiyuki Hiraga	Feb. 19, 2002
Residence (City, State & Country) JPY	CITIZENSHIP	
Settsu-shi, Osaka, Japan	Japan	
POST OFFICE ADDRESS (Complete Street Address including City, State & Country) c/o Yodogawa Works of DAIKIN INDUSTRIES, LTD., 1-1, Nishihitotsuya, Settsu-shi, Osaka 566-8585 Japan		

Full Name of Third Inventor, if any: see above

GIVEN NAME/FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
Masayuki NAMIMATSU	Masayuki Namimatsu	Feb. 20, 2002
Residence (City, State & Country) JPY	CITIZENSHIP	
Settsu-shi, Osaka, Japan	Japan	
POST OFFICE ADDRESS (Complete Street Address including City, State & Country) c/o Yodogawa Works of DAIKIN INDUSTRIES, LTD., 1-1, Nishihitotsuya, Settsu-shi, Osaka 566-8585 Japan		

Full Name of Fourth Inventor, if any: see above

GIVEN NAME/FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
Satoshi KOMATSU	Satoshi Komatsu	Feb. 20, 2002
Residence (City, State & Country) JPX	CITIZENSHIP	
Settsu-shi, Osaka, Japan	Japan	
POST OFFICE ADDRESS (Complete Street Address including City, State & Country) c/o Yodogawa Works of DAIKIN INDUSTRIES, LTD., 1-1, Nishihitotsuya, Settsu-shi, Osaka 566-8585 Japan		

Full Name of Fifth Inventor, if any: see above

GIVEN NAME/FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
Residence (City, State & Country)	CITIZENSHIP	
POST OFFICE ADDRESS (Complete Street Address including City, State & Country)		

*DATE OF SIGNATURE